1. INTRODUCTION

Ever since the first elucidation of coordination behaviour of transition metals by Alfred Werner in 1893, the field of coordination chemistry have grown tremendously. It led to the understanding of the synthesis, structure and reactivity of novel complexes and materials from simple metal-ligand complexes to organometallic catalysts and extended inorganic polymers. In recent decades two branches of coordination chemistry have emerged, one is Metal Organic Framework (MOFs) which consist of infinite networks or inorganic clusters bridged by simple organic linkers through metal-ligand coordination bonds and the other is supramolecular coordination complexes which consist of discrete systems in which carefully selected metal centres undergo self assembly with ligands containing multiple binding sites oriented with specific angularity to generate a finite supramolecular complex.[1] Supramolecular Chemistry over the past few decades has led to the synthesis of materials exhibiting unusual sensing, magnetic, optical, catalytic, drug delivery properties and for researchers investigating the structure and function of biomolecules. It represents an interdisciplinary field. Since the early pioneering work by Lehn[2] and Sauvage[3] on the feasibility and usefulness of coordination driven self assembly in the formation of infinite helicates, grids, ladders, racks, knots, rings, catenanes, rotaxanes and related species, several groups-those of Stang[4], Raymond[5], Fujita[6], Mirkin[7] Cotton[8] and others[9] - have independently developed and exploited novel coordination base paradigms for the self assembly of discrete metallacycles and metallacages with well defined shapes and sizes. The assembly of supramolecular ensembles depends on the information coded with the complementary building blocks that form the rigid framework of the architectures. The highly directional and predictable nature of the metal-ligand coordination sphere is a crucial feature of coordination driven self-assembly. With a growing knowledge of the synthesis and characterization of large, complex molecules, the past few years have seen a tremendous proliferation of new supramolecules and strategies to achieve complex topologies of the various developments in recent years using metal-ligand coordination, directional bonding, symmetry interaction, molecular panelling, weak link and dimetallic building block approach are the most extensively used and adopted.[10] These strategies have led to a wide variety of 2D and 3D molecular architectures of different shapes and sizes, which can be modulated though judicious choice of metal and ligands. In addition to that the functionalization of supramolecular assemblies has also been extensively investigated over the past few years with an aim to develop nanoscale ensembles that can find applications in diverse fields such biological

systems, host-guest chemistry, cavity-directed synthesis, catalysis, photonics, redox activity, magnetic behaviour, self-organization, and sensing.[10] However, almost all the coordination nanocages reported so far are hydrophobic, which greatly limits their applications in aqueous condition. We hypothesize this problem can be circumvented by turning these nanocages into colloids through surface functionalization with hydrophilic polymers and moreover if this supramolecular nanocages are designed in such a way that have pendant groups, it might be pave a facile way to incorporate a wide range of chemical functionalities on appropriate assemblies with further prospect of post-synthetic modification.

2. REVIEW OF LITERATURE

Supramolecular chemistry is a broad field, owing to the vast number of diverse structures that can be formed by using a variety of noncovalent intermolecular interactions. Notable examples include biologically relevant enzyme mimics[11], molecular devices including light harvesters[12], sensors[13], wires[14], and rectifiers[15], liquid crystals[16], molecular flasks[17], and more.[10] One subset of this chemistry is the self-assembly of coordination compounds. The discrete coordination-driven self-assemblies have received continuous attention due to their molecular architecture aesthetics and applications in recognition, catalysis, storage etc.[10] Functionalization of these supramolecules and post-assembly functionalization of metallosupramolecular prisms via covalent modifications to incorporate new functionalities under mild conditions[18] have been reported. The azide-alkyne-based "click" reactions are attractive alternatives in this context since they usually involve weakly polarized reactants, minimizing undesired side reactions, and thus could be an efficient method for expanding the range of chemical functionalities that can be tethered onto the metallosupramolecules. Post-synthetic modification of metal-organic frameworks[19] has been achieved in recent years through copper(I)-catalysed azide-alkyne cycloaddition (CuAAC) reactions.[20] Zhou et al.[21] described the functionalization of porous nanocages bearing free alkyne groups via the CuAAC reaction with azide-terminated PEG to transform the nanocages into water-stable colloids, which showed controlled release of the anticancer drug 5-fluorouracil. However, the use of CuAAC reactions in living systems is limited due the cytotoxicity of the Cu(I) catalyst toward living cells. Copper-free strain-promoted azide-alkyne cycloaddition (SPAAC) reactions [22] recently developed between cyclooctynes and azides have found wide utility in chemical biology. Use of these methodologies to functionalize three-dimensional

supramolecular cages, having large cavities, with biologically relevant homing devices may lead to better drug delivery devices. Recently, the first example of a Huisgen1,3-dipolar cycloaddition using an SCC scaffold was reported by Chakrabarty et. al. who utilized copper-free click chemistry on cyclooctyne-functionalized rhomboids.[23]

3. OBJECTIVES OF PRESENT STUDY

The main objective of this work will be to design definite supramolecular coordination complexes by using directional bonding approach and subsequently modify the complexes for surface functionalization to incorporate moieties that are amenable to further modification. In order to achieve these objectives, we propose to undertake the research in a phased manner and by identifying suitable targets as outlined below.

Firstly, organic ligands will be prepared with an aim to design ditopic, tritopic, tetratopic ligands having suitable pendant moiety that are amendable to further post synthetic modification. These ligands will be the starting material and key building block for the self-assembled coordination complexes. An important part of this work is the optimization of the different synthetic strategies that will be utilised for the synthesis. It may be mentioned that apart from synthesis, the compound prepared as part of this project will be analysed and completely characterized.

Secondly, the organic linkers would be studied to discover the possibility of organizing them into supramolecular ensembles by modulating their covalent and non-covalent interactions. This study will need elaborate studies using IR spectroscopy, fluorescence spectroscopy, NMR spectroscopy and mass spectroscopy (LC-MS) and single crystal X-ray diffraction.

Finally surface functionalization of the supramolecular complexes will be attempted with specific tags to attach organic moieties, which can be useful for targeted cell drug delivery purposes.

4. METHODOLOGY

As discussed earlier we shall be preparing functionalised supramolecular complexes, which will contain some tags for post synthetic modification. At the initial phase some organic ligands will be prepared and then they can be combined with metals to form supramolecular entity using metal nodes of Zn, Cd, Co, Pt, Pd etc. elements and then the functionalization of the supramolecular entity can be done by Huisgen type AAC reactions with a variety of functionalized azides to give functionalized metallacycles

under mild conditions. The azide alkyne based "click" reactions are attractive alternatives in this context since they usually involve weakly polarized reactants, minimizing undesired side reactions and thus could be an efficient method for expanding the range of chemical functionalities that can be tethered onto the supramolecular complex and can be use for drug delivery purpose as well.

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